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**Supplementary material for:**

**Stimuli responsive conductive polyaniline membrane:  
in-filtration electrical tuneability of flux and MWC0**

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### A. Membrane cells before assembling in the cross-flow rig

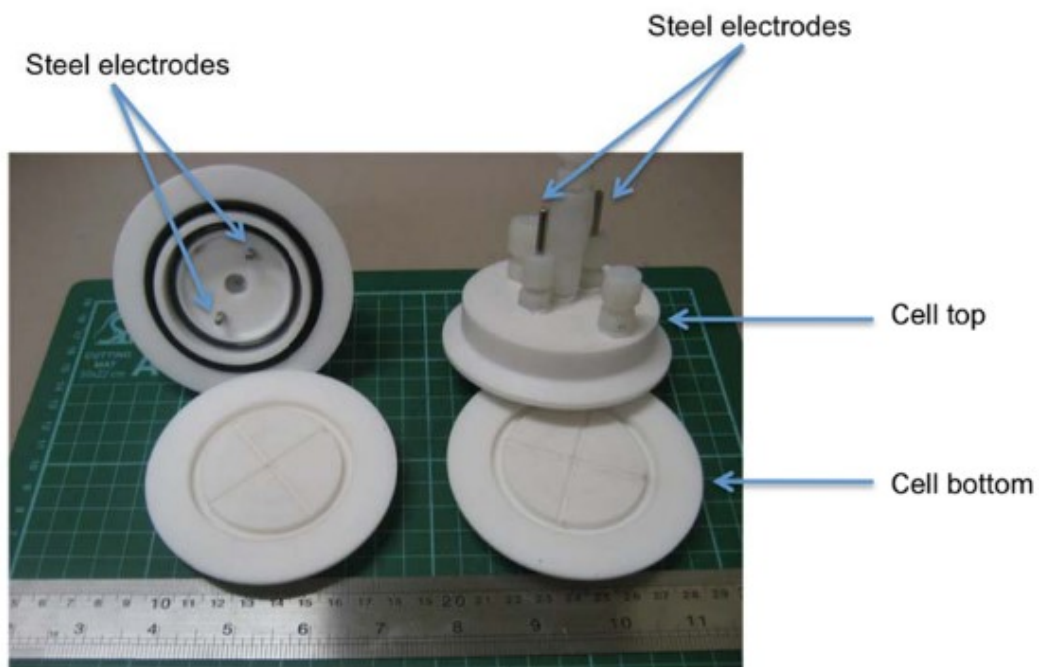


Fig SX1. Specially fabricated PTFE membrane cells before assembling in the cross-flow rig.

### B. Additional data for the PANI membrane properties

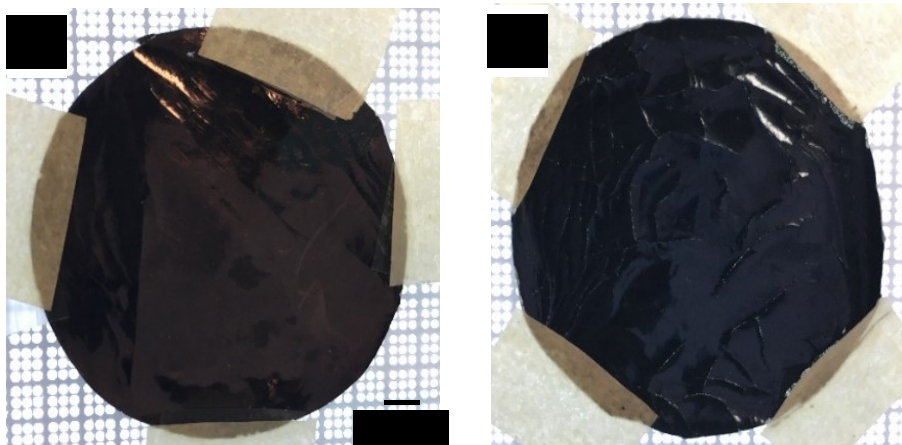


Fig SX2. Defects examination of membrane surfaces by light box: (a) Memb-EB-25 (purple bronze) and (b) Memb-ES-25 (dark green)

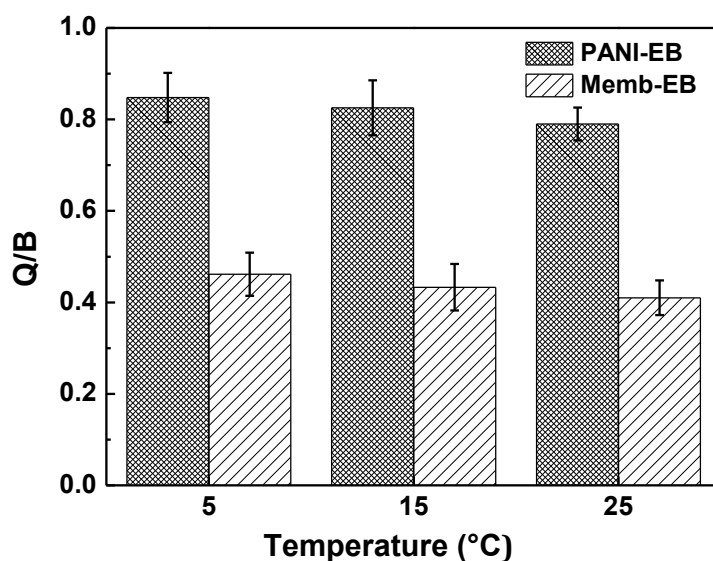


Fig SX3. Q/B (oxidation degree) of the PANI-EB and Memb-EB samples.

### C. Increasing the mechanical robustness of PANI membranes: effect of doping time

The PANI-ES membranes characterised prior to cross-flow testing far were sufficiently robust to handling and characterisation. However, it was found that the PANI-ES doped for 24 h were too brittle to survive the cross-flow testing. Therefore, the mechanical robustness of the membranes was examined to overcome this issue.

Doping time of the membrane determines the extent of the transformation of PANI-EB to the PANI-ES form and so in turn can influence the conductivity and tuneability of the PANI-ES membranes. Therefore, it was explored to determine if a lower doping time than is typical in the literature could be used to produce less brittle membranes. Currently, there is no clear information on this topic in the literature. To do this, Memb-EB-15 membranes were doped with 1.0 M HCl for 2, 6 and 24 h.

Mechanical testing of the Memb-ES-15 from the different doping times ([Table SX1](#)) showed that a doping time of 2 h gave the highest tensile strength and Young's modulus. % elongation decreased with increasing doping time.

FTIR spectra ([Fig SX4](#)) show no significant changes in the chemical structure of the PANI with doping time and conductivity was shown to be similar conductivity for all doping times ([Fig SX5](#)).

Therefore overall, doping time with HCl does not affect PANI membrane conductivity (which is directly related to membrane tuneability), but does effect mechanical properties. This may indicate that longer doping times disrupt the inter-polymer interactions (perhaps decreasing entanglement) rather than changing the PANI itself. The protonation of polyaniline doped by HCl is believed to give rise to a polaronic conduction band leading to a metallic state that enhances the conductivity of the PANI. The imine sites are believed to be protonated in preference, which gives the bipolaron form. However, this undergoes dissociation and

proportionate to form a delocalised polaron lattice or polysemiquinone form. It has been reported that the protonation consists of both chemical and diffusion processes [4]. The chemical reaction occurs between the proton in the aqueous acidic solution and the nitrogen atom on the imine unit of the PANI chains to form a polysemiquinone. On the other hand, diffusion processes correspond to diffusion of proton and counter-ions from an aqueous acidic solution into the membrane. Wan *et al.* reported that the doping processes at the initial stage were controlled by a chemical reaction, whereas the doping processes at the later stage were dominated by a diffusion processes [4]. In addition, it was found that the protonation processes become independent of the doping time when doping time is over a critical doping time – this would be when the chemical reaction is complete and sufficient diffusion has taken place to the doping sites. In the present case, we have thin membranes which would allow swift diffusion – allowing the acid to affect the inter-polymer interactions (making the polymer more brittle) once doping has completed. Thus, it can be concluded that the doping time of 2 h is already over the critical doping time of PANI membranes by 1.0 M HCl solution.

Therefore, considering the mechanical properties, electrical conductivity and FTIR results, it can be concluded that the doping time of 2 h is the best choice (not affecting key properties but making the membranes more mechanically robust) and therefore was selected as the minimum doping time for the membranes used in cross-flow testing.

Table SX1. Effect of doping time on the mechanical properties of the Memb-ES-15.

Doping time/h	Tensile strength /MPa	Young modulus/GPa	Elongation at break /%
2	10.1±0.19	1.23±0.031	0.028±0.002
6	8.29±0.27	1.07±0.062	0.026±0.001
24	8.31±0.1	0.89±0.045	0.019±0.001

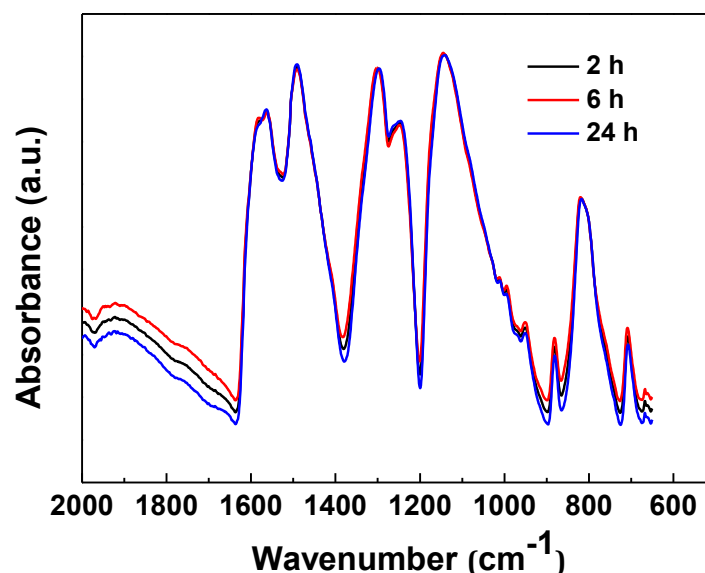


Fig SX4. FTIR of PANI Memb-ES-15 at different doping times (2, 6 and 24 h).

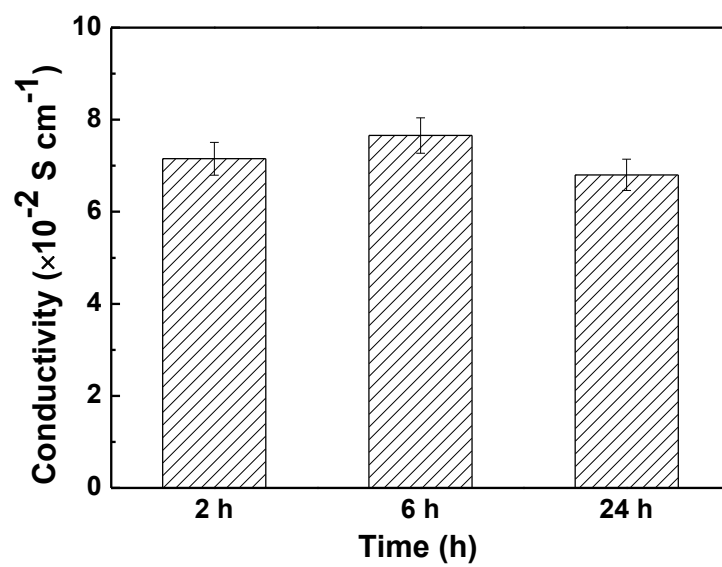


Fig SX5. The conductivity of Memb-ES-15 at different doping time (2, 6 and 24 h).

## D. Additional results for electrical tuneability of flux and MWCO in cross-flow filtration

Table SX2. MWCO change of membranes after filtration time of 120 min under applied potential.

Membrane	MWCO (g mol <sup>-1</sup> )		
	0 V	9 V	30 V
Memb-ES-5	>6,000	5,400±200	3,750±150
Memb-ES-15	>6,000	4,800±800	2,800±200

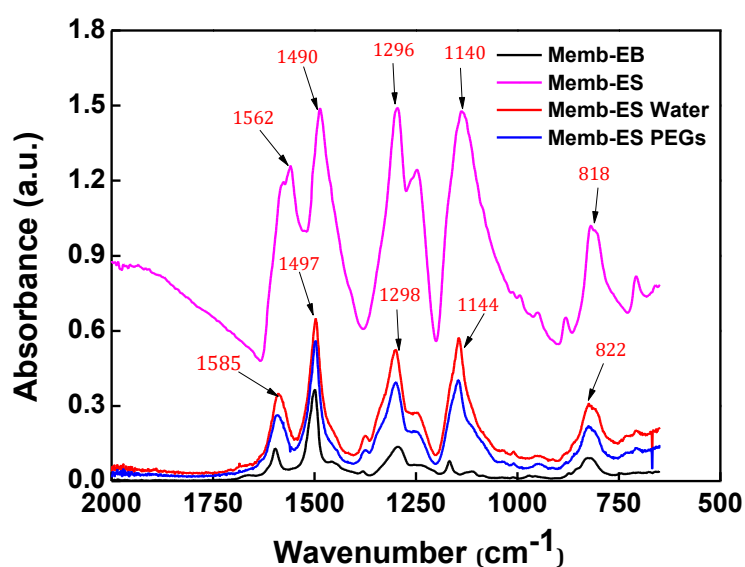


Fig SX6. FTIR spectra of membranes before and after cross flow filtration.

Table SX3. Colour characterisation of membranes before and after cross flow filtration.

Membrane	Red	Green	Blue
Memb-EB	12.6	18.8	18.4
Memb-ES	11.3	19.8	20.6
Memb-ES (Water)	12.0	19.9	20.5
Memb-ES (PEG UF)	12.0	20.1	20.9

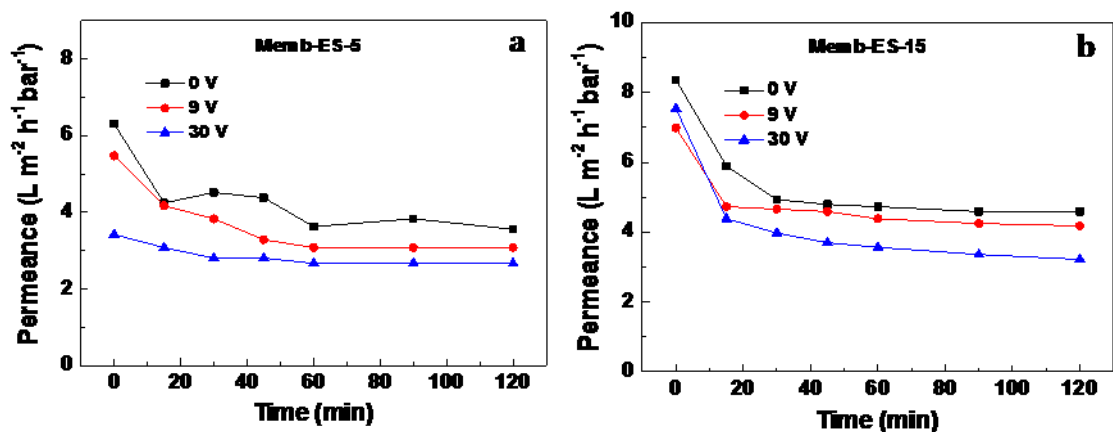


Fig SX7. Variation of PEG permeance of (a) Memb-ES-5 and (b) Memb-ES-15 under applied voltage from 0 V to 30 V (20 bar, 25°C, PEG).

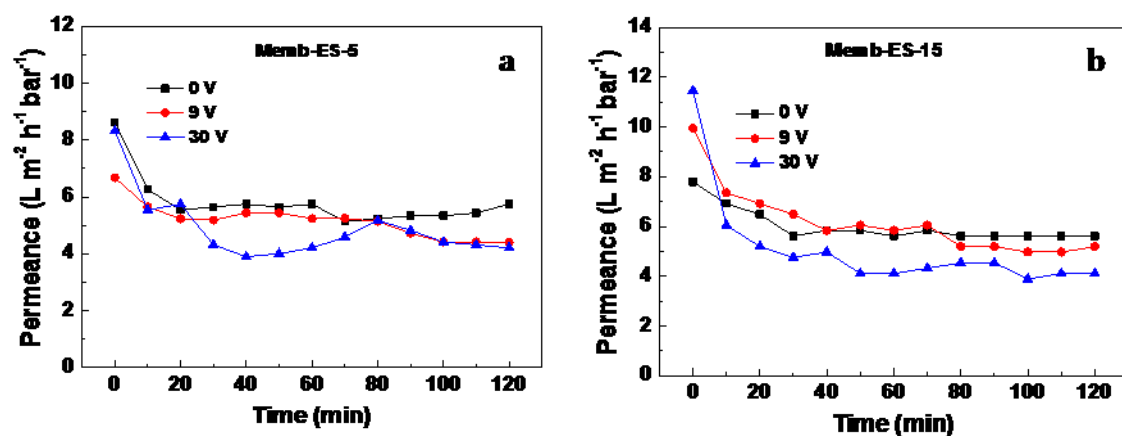


Fig SX8. Variation of water permeance of (a) Memb-ES-5 and (b) Memb-ES-15 under applied voltage from 0 V to 30 V (20 bar, 25°C, DI water).

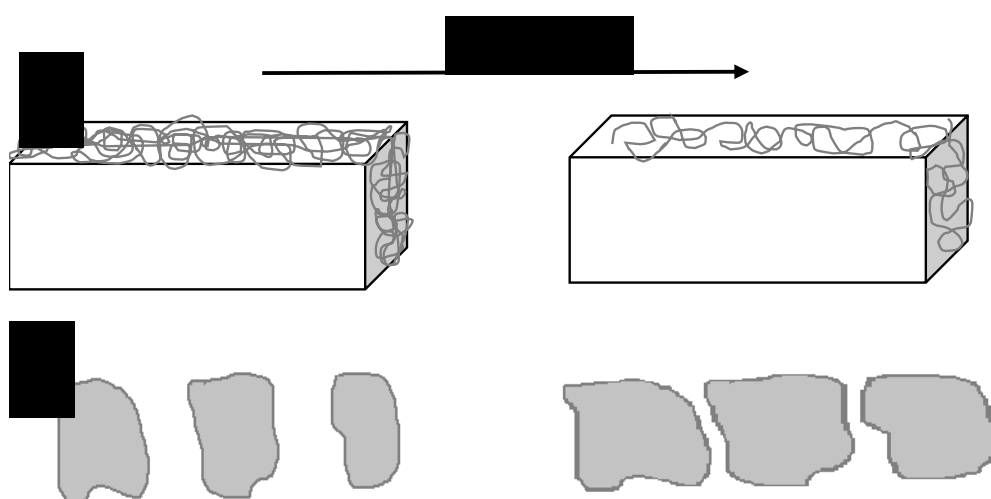


Fig SX9. Swelling of (a) dense and (b) porous membrane.



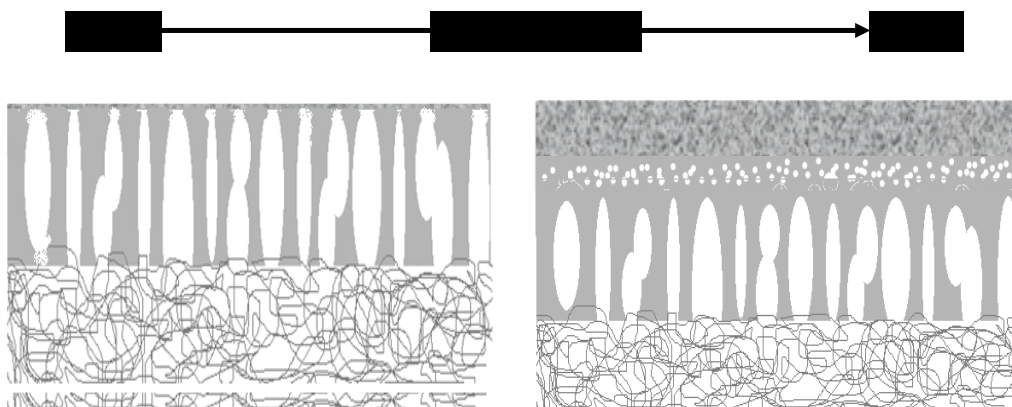


Fig SX10. Schematic representation of a nanofiltration membrane spectrum.

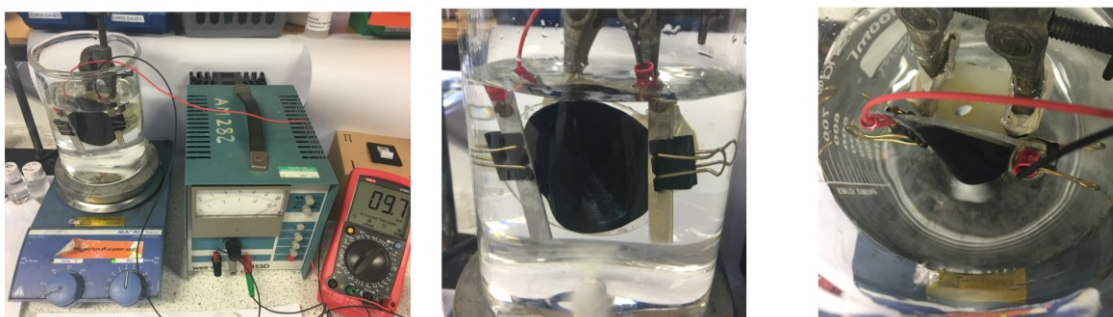


Fig SX11. Membrane swelling photos under applied potential

## References

- [1] M. Wan, J. Yang, Mechanism of proton doping in polyaniline, Journal of applied polymer science, 55 (1995) 399-405.